

The use of k_0 – NAA Standardization Technique in evaluating elements of significance for plant growth in the cultivated areas of Dutsin-Ma Local Government, Katsina State-Nigeria

Joseph, E.¹, Nasiru, R.², Sadiq, U.², Ahmed, Y. A.³

¹Department of Physics, Federal University, Dutsin-Ma, Katsina State, Nigeria

²Department of Physics, Ahmadu Bello University, Zaria, Nigeria

³Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria

Abstract: In this study, we have applied the k_0 –neutron activation analysis (k_0 – NAA) standardization technique to evaluate the concentration of various elements of significant for plant growth in the cultivated areas of Dutsin-Ma Local Government, Katsina State, North – West Nigeria. The samples and the standard reference material (NIST Coal Fly Ash 1633b) were irradiated at a thermal power level of 31.0 kW corresponding to a neutron flux setting of $2.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ and $5.0 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for the outer and inner irradiation channels respectively using the Nigeria Research Reactor – 1 (NIRR – 1). The result of the NIST Coal Fly Ash 1633b showed good agreement with the certified values using the k_0 -IAEA program. Besides, the concentration of twenty-six elements (Mg, Al, Ca, Ti, V, Mn, Dy, Na, K, As, Br, La, Sm, Sc, Cr, Fe, Co, Zn, Rb, Sb, Cs, Ba, Eu, Yb, Lu and Hf) were determined from 25 different samples collected within the study areas using the k_0 – IAEA program. The result shows that most of the trace elements required for plant growth are adequate, but elements like Mg and Ca are deficient, while Al, Mn and Fe, as well as the heavy metals (Cr and Zn) in most of the samples studied has reached toxic levels.

Keywords: Dutsin – Ma, k_0 – IAEA program, k_0 – INAA, NIRR – 1, plant growth

I. Introduction

The task of determining the concentration levels of the elemental mineral composition in geological samples particularly soil can be simplified by the use of reliable, simultaneous multi-element technique such as the instrumental neutron activation analysis (INAA) combined with high-resolution germanium gamma-ray spectrometry. In INAA technique, the elements to be measured in any given sample were made radioactive by irradiating the sample with neutrons. The number of detected gamma-rays of any particular energy is directly proportional to the disintegration rate of the radionuclide, which in turn also is directly proportional to the amount of parent isotope present in the sample [1][2].

Instrumental multi-element analytical technique, particularly the k_0 -Instrumental Neutron Activation Analysis technique (k_0 -INAA) which is a non-destructive and sensitive nuclear technique capable of accurate, quantitative analysis of a series of bulk and trace elements in various samples is most appropriate for a complex system like the soil. This technique in addition does not require prior sample preparation, [3][4], thus diminishing the risk of contamination or loss of certain elements that are vital to plant growth.

The recent implementation of the k_0 -NAA standardization technique to enhance [5] the Nigeria Research Reactor-1 (NIRR-1) which was designed and built by the China Institute of Atomic Energy (CIAE) [6] installed and commissioned at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria, for training and research among others is vital for multi-elemental studies. The detailed specification of NIRR – 1 has been described previously [7][8] as well as the neutron flux parameters characterization in the irradiation channels [7][9], the experimental protocols for the facilities [7] and calibration of the detectors at different source-detector geometries [7][8]. Also reported are the use of NIRR – 1 for relative quantitative NAA [11][12] and the k_0 –NAA standardization [13][14] technique for routine analysis in different samples.

This present work seeks to apply the k_0 – NAA standardization technique using the k_0 – IAEA software in the multi-elemental study of soil in order to appreciate roles played by different elements in plant growth. Although the trace elements in soil are very important for the quality of soil and environment, however excessive level of trace elements can cause pollution to waters, toxicity in plants, foods and ultimately in animals and humans that feed upon them [15][16][17]. The importance of mineral elements in human, animal and plant nutrition has been well recognized [18][19]. Deficiencies or disturbances in the nutrition of an animal cause a variety of diseases and can arise in several ways [20]. Despite this, studies on the elemental composition of soil at Dutsin-Ma Local Government Area, Katsina State, North – West Nigeria are non-existent to date and

therefore, very little is known about the distribution of various elements in the soil of this area, hence the need for this study.

II Materials and Methods

Sample Collection and Preparation

The soil samples were collected from twenty-five (25) different locations of the study area (figure 1) from the topsoil at a depth of 0-30cm using soil hand auger between distances of 2km to 5km. The soils were thoroughly mixed and transferred into clean and labeled plastic containers for analyses in the laboratory. The soil samples were prepared at the NAA sample preparation laboratory section, Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria for INAA irradiation. At first the samples were dried naturally at room temperature in a clean room and then oven dried at 105 °C to constant weight for 6 hours [21]; the oven dried material was crushed and sieved through a 150µm plastic mesh from which the representative sample was obtained [21][22]. The samples were placed in a high density polythene vials, and weighted using a METTLER TOLEDO balance model AE 240 with weights ranges between 150.0mg and 200.0mg were double heat-sealed. A total of 50 samples as well as the Standard Reference Material NIST Coal Fly Ash 1633b with certified values supplied by International Atomic Energy Agency (IAEA), Vienna, Austria used for the INAA method validation were also prepared for analysis by INAA.

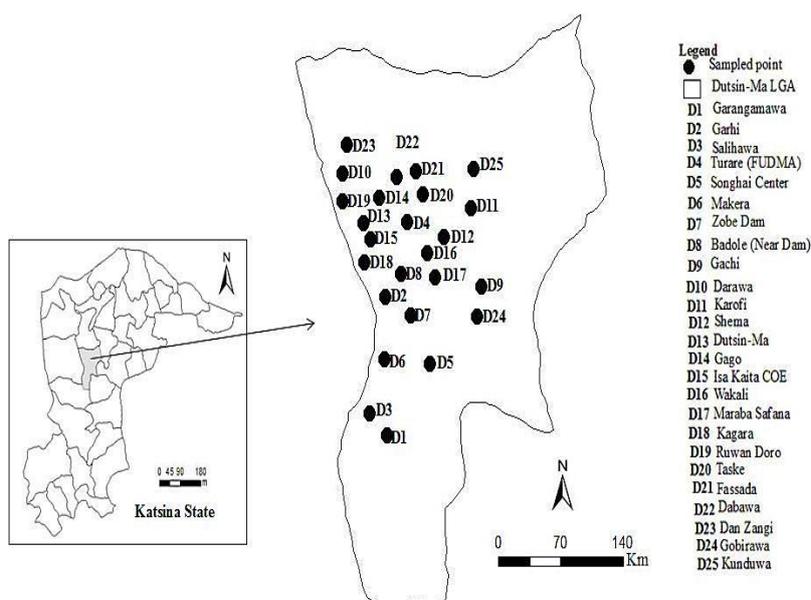


Figure 1: Map of Katsina State showing sample collection points

Sample Irradiation and Counting

The samples and standard were sent for irradiation into the reactor via the pneumatic transfer system for both the short-lived and the long-lived nuclides as described by [7][10]. The Nigeria Research Reactor-1 (NIRR-1) at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria which is a Miniature Neutron Source Reactor (MNSR) was used as the irradiation facility. The samples were irradiated for 60s (for the short-lived radionuclides) in the outer irradiation channel B4 and 6h (for the long-lived radionuclides) in the small irradiation channels A1, B2 and B3 of the same facility according to [10].

After the irradiation, the samples and standards were removed from the reactor and allowed to decay. The measurements were done using a high-purity coaxial germanium detector (HPGe) 30195 with relative efficiency of 30% and a resolution of 1.95 keV (FWHM) for the 1.33 MeV gamma line of ^{60}Co . The first and second counts for the short irradiation was carried out after irradiation at a detector-source distance of 15 cm for 600 seconds for the short-lived nuclides with a decay time of approximately 10 minutes, and at a detector-source distance of 2 cm for 600 seconds after allowing the samples to further decay for 3 hours for medium-lived nuclides respectively. Also, for the long irradiation, the first count was carried out after allowing the samples to decay for 3-4 days at a detector-source distance of 2 cm for 1800 seconds, while the second count was carried out at a detector-source distance of 2 cm for 3600 seconds one week after the first count. Samples were placed on plexi-glass sample holders mounted on the detector for the two counting geometries to ensure reproducible source positioning [23].

In order to establish the relationship between the peak energy and the probability of the detector recording a count in the full energy peak, we first calibrated the detector using k_0 -IAEA spectral analysis software. The detail of the calibration of the detector has been described by [24]. More so, for calculations of the elemental concentrations of the samples and the standard reference material, the k_0 -standardization technique using k_0 -IAEA spectral analysis software where the theory, methodology, recommended k_0 values and other related nuclear data has been described by different authors [25][26][27][28][29].

III. Results and Discussions

The sample history, the acquired spectrum showing the raw spectra, and the graphical interpretation of trace element concentration of the standard reference material and that of one the samples as well as the concentrations of the various elements in the NIST Coal Fly Ash 1633b and the twenty-five samples determined are presented. The standards and all the samples were routinely analyzed, writing to peak areas, interpreted and the final result reported. Our samples which were regarded as ordinary samples and the standard reference material spectra were all interpreted simultaneously using the k_0 – IAEA software program.

The results of NIST Coal Fly Ash 1633b is purely intended to validate the accuracy of the technique. From the results presented on table 1, it is evident that there is a good agreement, consistency with the values obtained in our work and that of the certified values when considering that the ratio of most of the values obtained to the certified values tend to unity. Based on this, we can therefore conclude that our methodology can be applied in the determination of the elemental composition of geological matrix such as soil. A total of twenty-six (26) elements were determined from the twenty-five (25) samples collected from different location at Dutsin-Ma local government area, Katsina State. Most of these elements have biological functions in plants and some animals but the essentiality of some of them for humans and their requirements are still under research [30]. We have briefly described some of these elements that are significant in plant growth as well as others that are toxic to plants and animals.

Table 1: Sample History for SRM Coal Fly Ash 1633b

History of sample: 1 (NIST 1633b)

Sep 15 2013 12:00:0.000: 0.164 mg of sample packaged in recipient 1 (10mm_1)
Sep 26 2013 10:18:0.000 (06h00): in NIRR-1 CHANNEL A1 at unknown flux
Sep 30 2013 16:11:31.000 (32'57.000): with GEM 30195 at 20.0 mm
Oct 8 2013 13:20:59.000 (01h01): with GEM 30195 at 20.0 mm
Dec 10 2013 12:58:0.000 (01'00.000): in NIRR-1 CHANNEL B4 at unknown flux
Dec 10 2013 13:39:0.000 (10'02.000): with GEM 30195 at 150.0 mm
Dec 10 2013 15:53:59.000 (10'07.000): with GEM 30195 at 20.0 mm
Dec 15 2014 12:00:0.000: sample unpacked from recipient 1 (10mm_1)

Table 2: Sample History for DTM 15

History of sample: 2 (DTM 15)

Sep 15 2013 12:00:0.000: 0.180 mg of sample packaged in recipient 1 (10mm_1)
Oct 24 2013 10:28:0.000 (06h00): in NIRR-1 CHANNEL B3 at unknown flux
Oct 28 2013 11:34:14.000 (31'32.000): with GEM 30195 at 20.0 mm
Nov 3 2013 11:34:0.000 (01h00): with GEM 30195 at 20.0 mm
Dec 10 2013 13:50:0.000 (01'00.000): in NIRR-1 CHANNEL B4 at unknown flux
Dec 10 2013 14:03:0.000 (10'04.000): with GEM 30195 at 150.0 mm
Dec 10 2013 16:37:59.000 (10'08.000): with GEM 30195 at 20.0 mm
Dec 15 2014 12:00:0.000: sample unpacked from recipient 1 (10mm_1)

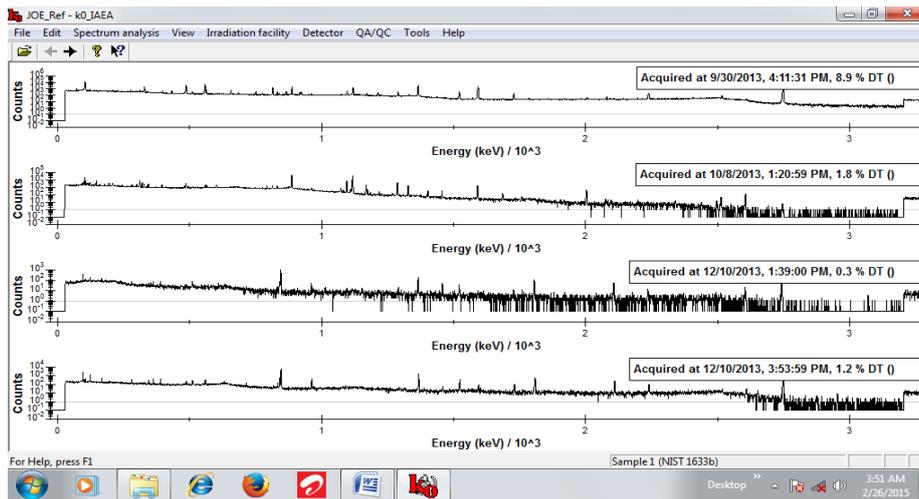


Figure 2: Acquired Spectrum for NIST 1633b showing all four Raw Spectra

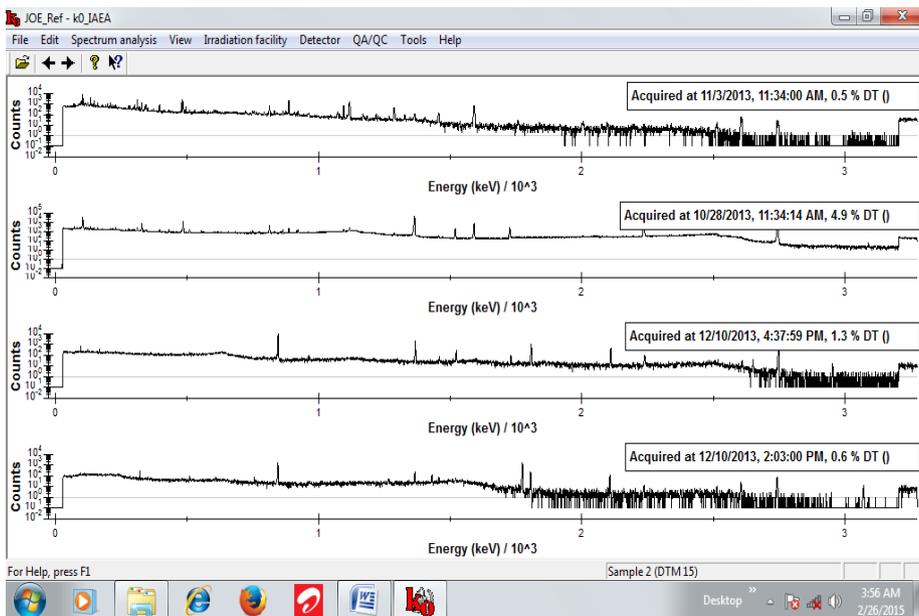


Figure 3: Acquired Spectrum for DTM 15 showing all four Raw Spectra

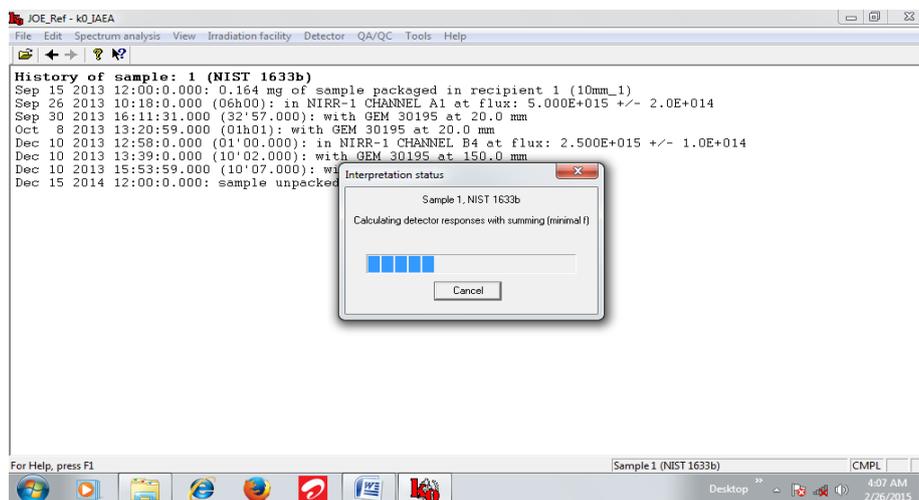


Figure 4: Graphical interpretation of trace element concentration for NIST 1633b

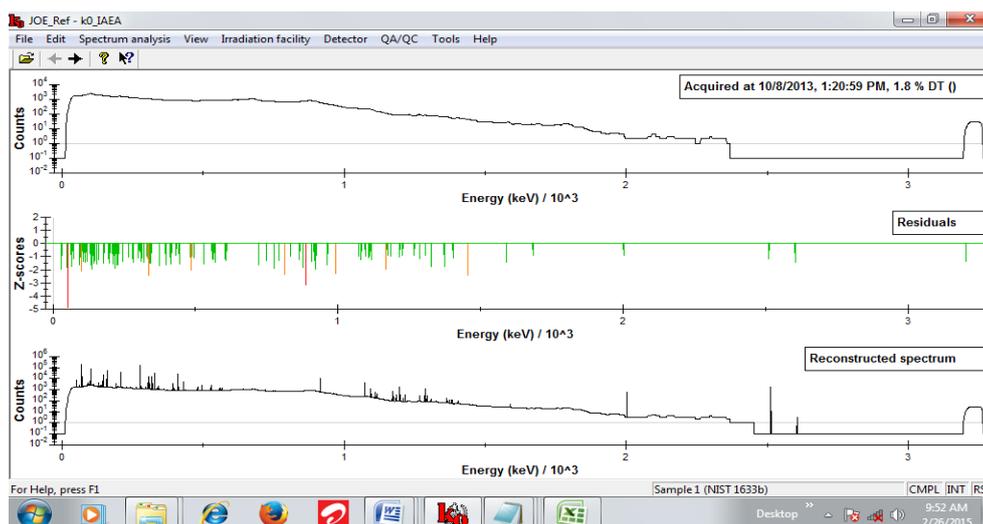


Figure 5: Graphical interpretation of trace element concentration for NIST 1633b

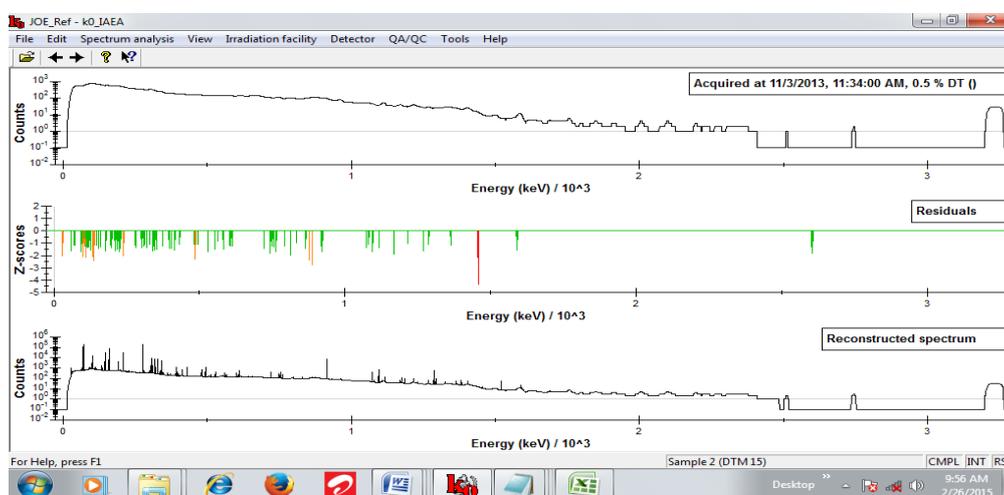


Figure 6: Graphical interpretation of trace element concentration for DTM 15

Mg was measured in only five (5) samples ranging from 1221 ± 197 to 2281 ± 385 mg/kg which is low and this might be as a result of the high acidic nature of the investigated soil. Mg plays a major role in the production of chlorophyll, on which photosynthesis depends and also activates many enzymes [31]. It has been reported that Mg appears to be associated with protein synthesis via its roles in ribosomal structure and function [32]. In leaves, the MRS2-11 transporter is thought to facilitate Mg entry to the chloroplast [33], where between 15 and 20% of the Mg in leaves is associated with chlorophyll [32]. Because Mg is a phloem-mobile element, it is readily translocated to fruit, seed and tubers [32], and its involvement in the metabolism of calcium [34][35][36].

The concentrations of Al in the soil were found in the range of 20640 ± 289 to 57890 ± 463 mg/kg is measured in all the samples. This is expected because Al is found at easily measurable levels in various biological fluids and tissues [37]. Plants sensitive to Al toxicity have greatly reduced yield and crop quality [38][39][40], and besides, Al causes extensive root injury, leading to poor ion and water uptake [41].

Ca was measured in only eight (8) samples with concentration ranging from 2029 ± 485 to 7851 ± 1186 mg/kg and is indicative of the fact that Ca is less available to plant within our area of study. According to [42], Ca has a major role in the formation of the cell wall membrane and its plasticity, affecting normal cell division by maintaining cell integrity and membrane permeability. It is also an activator of several enzyme systems in protein synthesis and carbohydrate transfer, as well as being essentials for seed production in many plants [42]. The growing tips of roots and leaves turn brown and die as a result of Ca deficiency and also limit plant growth.

The average concentration of Ti obtained ranges from 1894 ± 244 to 4324 ± 311 mg/kg. Though, Ti is not an essential element for plant nutrition and no clear evidence of a biochemical role of Ti has been reported, but

according to Chapman, [43] it has catalytic function in nitrogen fixation by symbiotic microorganisms and in photooxidation of nitrogen compounds by higher plants and particular processes of photosynthesis. The concentration of Dy was determined in all the samples with range from 2.1 ± 0.4 to 7.9 ± 0.5 mg/kg, even though it should have the concentration range of 3.8 to 5.0 mg/kg in soil [44][45].

Though, low concentration of V is beneficial to microorganisms, animals, and higher plants [46]. However, according to [47], it is toxic to humans and other animals. In this study, V was determined in all the samples ranging from 13 ± 2 to 60 ± 7 mg/kg. Mn is a micronutrient whose concentration in plants enhances its growth [48]. It was measured in all our samples ranging between 98 ± 1 and 336 ± 2 mg/kg. Mn acts as an activator and constituent of many enzymes present in humans [49] and so is an essential element for humans [50].

The Cr concentrations in the soil were found in the range of 18 ± 4 mg/kg to 112 ± 9 mg/kg. All the measured concentrations of Cr in our samples exceeded the permissible limit for plants of 1.30 mg/kg recommended by WHO, though within the world background report (7 – 221 mg/kg), while some are above the range of the US permissible limit of 20 to 85 mg/kg [51]. Also, Co is significant for plant growth but can be toxic at elevated levels. It was determined in twenty-four samples with a range of 2.0 ± 0.2 to 17.2 ± 0.1 mg/kg. Co essentiality has been shown but its deficiency inhibits some elements in plant growth.

The concentration of zinc in our samples measured ranged from 18 ± 5 to 98 ± 7 mg/kg. Zinc toxicity depends on pH, which controls the concentration of zinc in solution. High concentrations of zinc can cause toxicity in plants [52]. The general symptoms are stunting of shoot, curling and rolling of young leaves, death of leaf tips and chlorosis. Zinc though an essential element for plant growth, showed toxicity symptoms at higher concentrations inhibiting root growth [53][54]. It has been reported that the nitrogen and phosphorous increased with the increase in zinc content in the roots [55]. The concentration of zinc in the roots decreased with plant age as reported by [56].

The concentration of As in our samples measured range from 0.44 ± 0.09 to 3.4 ± 0.18 mg/kg, implying that only two (2) of our samples are above the maximum permissible limit of 2 mg/kg set by WHO [51]. We must state here that As is seriously toxic when it is greater or equal to 5 mg/kg. Arsenic is regarded as a human carcinogen from extremely low levels of exposure, having no possible beneficial metabolic functions for humans [37].

K has many functions in plant growth. It was measured in all our samples in large amount. It is essential for photosynthesis, activates enzymes to metabolize carbohydrates for the manufacture of amino acids and proteins, facilitates cell division and growth by helping to move starches and sugars between plant parts, adds stalk and stem stiffness, increases disease resistance, increases drought tolerance, regulates opening and closing of stomates, gives plumpness to grain and seed, improves firmness, texture, size and color of fruit crops and increases the oil content of oil crops [57]. However, deficiency in plants exhibit chlorosis (loss of green color) along the leaf margins or tips starting with the bottom leaves and progressing up the plant, among others [57].

Fe which is also significant in plant growth was measured in all our samples ranging from 7261 ± 170 to 361534 ± 255 mg/kg. The essential role of Fe in plant biochemistry includes the mechanisms of photosynthetic electron transfer, influencing chlorophyll formation, nucleic acid metabolism, redox reactions of chloroplasts, mitochondria, and peroxisomes, amongst others [58]. Also, according to [58], Fe deficiency affects several physiological processes and therefore retards plant growth as well as plant yield.

IV. Conclusion

The k_0 – IAEA software program has been used in this study to measure the concentration of twenty – six (26) elements from twenty – five (25) cultivated locations at Dutsin-Ma Local Government Area of Katsina State. The elements are Mg, Al, Ca, Ti, V, Mn, Dy, Na, K, As, Br, La, Sm, Sc, Cr, Fe, Co, Zn, Rb, Sb, Cs, Ba, Eu, Yb, Lu and Hf. Our study shows that most of the essential elements which are significant for plant growth are adequate in the soil to enable proper growth of plant particularly cereals, but the heavy metals particularly Cr and Zn is at the toxic level, hence they are source of soil pollution. Finally, with the information on the elemental composition from this study area, farmers and other relevant agencies involved in planning as it regard agricultural practices can be properly guided on the utilization of the soil.

Acknowledgment

The authors are grateful to the Centre for Energy Research and Training, Ahmadu Bello University, Zaria for allowing us access to use their facility for this work.

Table 3: Analytical results of NIST Coal Fly Ash 1633b (in mg/kg, unless otherwise stated)

Element	Certified Value	ThisWork	Ratio (Expt./Cert. Value)
Al	150500 ± 2700	149700±410	0.99
As	136.2 ± 2.6	135.7±0.3	1.00
Ba	709 ± 27	710±17	1.00
Ca	15100 ± 600	15000±812	0.99
Ce	190*	182±21	0.96
Co	50*	41.34±0.9	0.83
Cr	198.2 ± 4.7	194±6	0.98
Cs	11*	10.4±0.23	0.95
Eu	4.1*	3.2±0.3	0.78
Fe	77800 ± 2300	77820±300	1.00
Hf	6.8*	5.9±1.3	0.87
Ho	3.5*	3.1±0.67	0.89
K	19500 ± 300	19500±612	1.00
La	94*	93±0.55	0.99
Mg	4820 ± 80	4911±200	1.02
Mn	131.8 ± 1.7	134.1±3.1	1.02
Na	2010 ± 30	2180±28.3	1.08
Ni	120.6 ± 1.8	120.8±7.4	1.00
Sr	1041 ± 14	1041±26	1.00
Ta	1.8*	1.9±0.9	1.06
Tb	2.6*	2.5±0.32	0.96
Th	25.7 ± 1.3	24.9±3	0.97
U	8.79 ± 0.36	8.9±0.14	1.01
V	295.7 ± 3.6	297.1±4.1	1.00
Yb	7.6*	7.4±0.7	0.97
Zn	210*	201±6	0.96

*: Non certified/recommended value

TABLE 4: CONCENTRATIONS OF VARIOUS ELEMENTS IN SOILS INVESTIGATED (IN MG/KG, UNLESS OTHERWISE STATED)

ELEMENT	DTM 01	DTM 02	DTM 03	DTM 04	DTM 05
Mg	ND	1885± 601	1221±197	1861 ± 539	ND
Al	21000 ± 500	42683 ± 409	28110 ± 291	36621 ± 470	23679 ± 190
Ca	ND	ND	3350 ± 514	3232±978	ND
Ti	1971 ± 370	3680 ± 114	2621 ± 230	3492 ± 381	2403 ± 391
V	18 ± 9.5	40 ± 4	35 ± 1	38.3 ± 1.9	54 ± 7
Mn	118.1 ± 2.4	192 ± 3	202 ± 24	135 ± 7	157 ± 5
Dy	3.0 ± 0.01	5.94 ± 1.0	6.2 ± 0.9	3.9 ± 0.25	2.5 ± 0.22
Na	870 ± 21	594 ± 12	2651 ± 15	2366 ± 17	435 ± 7
K	7961 ± 781	9072 ± 119	8664 ± 160	11523 ± 265	4418 ± 530
As	0.52 ± 0.01	0.85 ± 0.17	0.5 ± 0.11	0.98 ± 0.35	3.4 ± 0.18
Br	0.66 ± 0.20	2.01 ± 0.11	1.1 ± 0.1	1.30 ± 0.18	0.85 ± 0.76
La	23.19 ± 0.18	32.01 ± 0.67	31.12 ± 0.29	44.21 ± 0.11	19.1 ± 0.9
Sm	3.38 ± 0.19	5.47 ± 0.8	6.30 ± 0.42	7.60 ± 0.24	2.67 ± 0.12
Sc	2.92 ± 0.16	7.51 ± 0.41	4.4 ± 0.01	5.61 ± 0.19	3.34 ± 0.25
Cr	48 ± 8	112 ± 9	28 ± 4	53 ± 1	52 ± 3
Fe	7261 ± 170	92227 ± 255	10760 ± 400	14880 ± 971	361534 ± 255
Co	3.7 ± 0.1	17.2 ± 0.1	4.2 ± 0.7	5.63 ± 0.55	6.9 ± 0.76
Zn	19 ± 1	64 ± 3	31 ± 9	51 ± 7	36±11
Rb	30 ± 4	69 ± 14	33 ± 2.5	58 ± 5	39 ± 4
Sb	ND	ND	ND	1.21 ± 0.4	0.16 ± 0.21
Cs	1.9 ± 1.0	4.8 ± 0.5	1.9 ± 0.2	2.0 ± 0.1	1.5 ± 0.13
Ba	381 ± 35	841 ± 66	280 ± 37	362 ± 48	227 ± 83
Eu	0.70 ± 0.23	0.86 ± 0.11	ND	ND	ND
Yb	3.13 ± 0.15	3.5 ± 0.1	3.5 ± 0.19	3.0 ± 0.1	1.9 ± 0.15
Lu	0.26 ± 0.01	0.50 ± 0.1	0.43 ± 0.21	0.40 ± 0.05	0.2 ± 0.01
Hf	ND	24.8 ± 0.11	ND	24.4 ± 0.7	22.7 ± 0.32

TABLE 4: CONCENTRATIONS OF VARIOUS ELEMENTS IN SOILS INVESTIGATED (IN MG/KG, UNLESS OTHERWISE STATED) (CONTINUED)

ELEMENT	DTM 06	DTM 07	DTM 08	DTM 09	DTM 10
Mg	ND	ND	ND	ND	ND
Al	57890 ± 900	27222 ± 210	21541 ± 432	46145 ± 781	29112 ± 320
Ca	2439 ± 901	ND	ND	ND	ND
Ti	4324 ± 311	ND	3363 ± 400	3420 ± 381	3667 ± 565
V	54 ± 4	27.7 ± 1.0	20 ± 8	60 ± 7	16.2 ± 2.2
Mn	ND	115 ± 6	174 ± 5	258 ± 16	153 ± 45
Dy	6.1 ± 0.7	2.8 ± 0.8	3.4 ± 0.33	4.5 ± 0.12	3.0 ± 0.46
Na	431 ± 6	1247±51	1313 ± 8	1657 ± 32	2723 ± 7.1
K	3361 ± 232	15990 ± 111	10460 ± 789	12090 ± 190	28940 ± 281
As	1.5 ± 0.5	3.2 ± 0.3	0.96 ± 0.45	0.7 ± 0.19	0.93 ± 0.23
Br	2.5 ± 0.1	0.93 ± 0.1	1.5 ± 0.15	1.5 ± 0.2	0.97 ± 0.09
La	ND	22.51 ± 0.15	87.0 ± 0.1	77.2 ± 0.5	25.1 ± 0.5
Sm	4.77 ± 0.11	3.64 ± 0.72	ND	13.00± 0.19	ND
Sc	7.2 ± 0.03	2.94± 0.23	3.8 ± 0.55	8.4 ± 0.9	3.28 ± 0.07
Cr	65 ± 4	54 ± 6	38 ± 3	51.6 ± 2.9	22.6 ± 2.5
Fe	30570 ± 306	22349 ± 258	10270 ± 216	23060 ± 988	11380 ± 230
Co	9.4 ± 0.1	D4.9 ± 0.2	ND	ND	2.5 ± 0.5
Zn	30 ± 6	26 ± 3	25 ± 9	32 ± 2	27±7
Rb	27 ± 3	39 ± 9	53 ± 7	63 ± 6	135 ± 9
Sb	0.15 ± 0.2	0.19 ± 0.02	0.14 ± 0.09	ND	ND
Cs	2.0 ± 0.8	1.6 ± 0.8	1.3 ± 0.8	3.0 ± 0.4	2.3 ± 0.2
Ba	188 ± 32	876 ± 45	432 ± 37	362 ± 36	666 ± 32
Eu	0.8 ± 0.3	0.6 ± 0.6	0.6 ± 0.3	1.1 ± 0.3	0.6 ± 0.8
Yb	3.9 ± 0.52	2.2 ± 0.5	2.82 ± 0.5	4.8 ± 0.8	3.16 ± 0.87
Lu	0.31 ± 0.06	0.30 ± 0.07	0.39 ± 0.12	0.59 ± 0.1	0.27 ± 0.01
Hf	21.7 ± 0.5	23.6 ± 0.9	32.6 ± 0.12	24.30 ± 0.77	34.7 ± 0.45

TABLE 4: CONCENTRATIONS OF VARIOUS ELEMENTS IN SOILS INVESTIGATED (IN MG/KG, UNLESS OTHERWISE STATED)(CONTINUED)

ELEMENT	DTM 11	DTM 12	DTM 13	DTM 14	DTM 15
Mg	ND	ND	ND	ND	ND
Al	22160 ± 421	20640 ± 289	38670 ± 425	26920 ± 215	26910 ± 404
Ca	ND	ND	ND	2029 ± 485	7851 ± 1186
Ti	2647 ± 365	1894 ± 244	3072 ± 276	4242 ± 432	3412 ± 376
V	17 ± 2	13 ± 2	33 ± 4	18.4 ± 1.6	24 ± 3
Mn	100 ± 1	104 ± 1	231 ± 1	259 ± 4	191 ± 1
Dy	2.5 ± 0.2	3.4 ± 0.3	3.8 ± 1.4	3.4 ± 0.3	3.2 ± 0.2
Na	1207 ± 4	2327 ± 4.654	2224 ± 4	3219 ± 6	2318 ± 9
K	13070 ± 183	12870 ± 193	15920 ± 207	14540 ± 203	10490 ± 178
As	0.7 ± 0.1	0.5 ± 0.1	1.3 ± 0.1	ND	ND
Br	0.44 ± 0.09	0.8 ± 0.1	1.0 ± 0.1	0.9 ± 0.2	0.90 ± 0.13
La	27.24 ± 0.14	25.8 ± 0.2	31.5 ± 0.2	31.6 ± 0.2	22.3 ± 0.1
Sm	3.09 ± 0.02	4.01 ± 0.02	5.54 ± 0.02	5.10 ± 0.03	3.57 ± 0.02
Sc	2.47 ± 0.04	2.90 ± 0.04	4.21 ± 0.05	3.88 ± 0.05	3.1 ± 0.1
Cr	13 ± 2	16 ± 2	20 ± 2	32 ± 2	14.5 ± 1.5
Fe	9359 ± 197	8450 ± 177	16020 ± 240	13370 ± 227	9923 ± 208
Co	2.2 ± 0.3	2.5 ± 0.2	5.5 ± 0.3	3.9 ± 0.3	3.1 ± 0.2
Zn	19 ± 6	BDL	98 ± 7	44 ± 6	45 ± 5
Rb	74 ± 5	68 ± 5	86 ± 5	68 ± 6	54 ± 4
Sb	ND	ND	0.23 ± 0.04	0.11 ± 0.06	ND
Cs	1.3 ± 0.2	1.1 ± 0.7	2.3 ± 0.27	1.7 ± 0.2	ND
Ba	ND	322 ± 39	374 ± 25	ND	ND
Eu	0.5 ± 0.12	0.55 ± 0.23	0.88 ± 0.34	0.8 ± 0.19	0.63 ± 0.19
Yb	2.5 ± 0.15	ND	ND	ND	2.70 ± 0.33
Lu	0.31 ± 0.21	0.20 ± 0.01	0.52 ± 0.07	0.39 ± 0.05	0.30 ± 0.08
Hf	21.6 ± 0.1	28.1 ± 0.6	24.4 ± 0.9	31.4 ± 0.7	ND

TABLE 4: CONCENTRATIONS OF VARIOUS ELEMENTS IN SOILS INVESTIGATED (IN MG/KG, UNLESS OTHERWISE STATED)(CONTINUED)

ELEMENT	DTM 16	DTM 17	DTM 18	DTM 19	DTM 20
Mg	ND	ND	ND	ND	ND
Al	22200 ± 490	28210 ± 250	30470 ± 980	30370 ± 400	56620 ± 943
Ca	ND	3073 ± 680	ND	ND	ND
Ti	3187 ± 280	2564 ± 261	3350 ± 970	3346 ± 540	4131 ± 765
V	23 ± 3	38 ± 2	40 ± 3.2	23 ± 9	36 ± 8
Mn	200 ± 18	210 ± 11	282 ± 27	254 ± 24	211 ± 6
Dy	2.1 ± 0.4	4.4 ± 0.35	6.5 ± 0.7	4.9 ± 0.5	6.6 ± 0.3
Na	1208 ± 21	2951 ± 10	2038 ± 76	1246 ± 71	ND
K	8800 ± 120	10260 ± 460	9102 ± 173	9103 ± 364	13450 ± 202
As	1.9 ± 0.7	ND	ND	1.2 ± 0.11	1.3 ± 0.17
Br	1.0 ± 0.1	1.61 ± 0.18	1.2 ± 0.9	1.3 ± 0.1	1.3 ± 0.2
La	ND	25.8 ± 0.2	24.4 ± 0.19	25 ± 0.2	57.8 ± 0.23
Sm	ND	4.39 ± 0.28	3.99 ± 0.21	3.94 ± 0.97	9.01 ± 0.33
Sc	3.78 ± 0.34	4.95 ± 0.4	5.70 ± 0.9	4.33 ± 0.01	7.3 ± 0.8
Cr	49 ± 3	32 ± 1	39 ± 7	18 ± 4	29 ± 7
Fe	19080 ± 400	13670 ± 739	14652 ± 231	13000 ± 892	21660 ± 998
Co	4.4 ± 0.5	5.5 ± 0.31	5.7 ± 0.3	ND	ND
Zn	18 ± 5	ND	50 ± 6	24 ± 5	26 ± 8.4
Rb	39 ± 3.9	48 ± 5.6	53 ± 5	52 ± 5	86 ± 9
Sb	0.16 ± 0.23	ND	ND	ND	ND
Cs	1.1 ± 0.34	1.3 ± 0.26	2.4 ± 0.7	2.6 ± 0.44	5 ± 0.9
Ba	ND	ND	ND	327 ± 34	377 ± 30
Eu	0.54 ± 0.09	0.7 ± 0.1	0.7 ± 0.1	1.0 ± 0.1	1.5 ± 0.2
Yb	2.3 ± 0.1	1.8 ± 0.1	3.2 ± 0.1	2.99 ± 0.13	4.1 ± 0.2
Lu	0.83 ± 0.09	0.37 ± 0.02	0.42 ± 0.05	0.41 ± 0.09	0.47 ± 0.06
Hf	21.5 ± 0.6	18.7 ± 0.3	20.4 ± 0.5	35.9 ± 0.9	27.2 ± 0.9

TABLE 4: CONCENTRATIONS OF VARIOUS ELEMENTS IN SOILS INVESTIGATED (IN MG/KG, UNLESS OTHERWISE STATED)(CONTINUED)

ELEMENT	DTM 21	DTM 22	DTM 23	DTM 24	DTM 25
Mg	ND	ND	2281 ± 385	2177 ± 494	ND
Al	22330 ± 313	35860 ± 466	37880 ± 417	33980 ± 442	34900 ± 349
Ca	ND	ND	ND	3229 ± 685	2993 ± 694
Ti	3007 ± 235	2060 ± 356	2824 ± 285	3573 ± 375	1950 ± 296
V	19 ± 2	18 ± 3	51 ± 3	43 ± 3	18 ± 3
Mn	98 ± 1	135 ± 1	205 ± 1	336 ± 2	165 ± 2
Dy	2.9 ± 0.2	3.3 ± 0.5	5.5 ± 0.3	4.3 ± 0.3	7.9 ± 0.5
Na	116 ± 7	1464 ± 4	2212 ± 4	1717 ± 2	3508 ± 11
K	13070 ± 500	16930 ± 398	11650 ± 980	8648 ± 100	22610 ± 740
As	0.9 ± 0.1	1.02 ± 0.09	0.6 ± 0.1	0.63 ± 0.08	0.4850 ± 0.1
Br	0.8 ± 0.1	0.8 ± 0.1	1.5 ± 0.1	2.1 ± 0.5	1.0 ± 0.2
La	21.05 ± 0.12	27 ± 0.1	56.9 ± 0.2	27.2 ± 0.1	53.3 ± 0.2
Sm	2.90 ± 0.01	3.16 ± 0.02	9.8 ± 0.03	4.77 ± 0.02	6.29 ± 0.03
Sc	3.41 ± 0.04	2.67 ± 0.04	5.91 ± 0.06	7.99 ± 0.07	2.99 ± 0.04
Cr	19.42 ± 1.5	14 ± 2	56 ± 2	50 ± 2	22 ± 2
Fe	7322 ± 161	7659 ± 168	18900 ± 240	21290 ± 491	8807 ± 644
Co	2.0 ± 0.2	2.5 ± 0.2	6.1 ± 0.3	8.787 ± 0.3076	3.7 ± 0.3
Zn	ND	22 ± 5	31 ± 6	70 ± 7	31 ± 5
Rb	52 ± 3	66 ± 4	66 ± 4	50 ± 4	77 ± 5
Sb	0.13 ± 0.03	0.13 ± 0.04	0.15 ± 0.04	0.24 ± 0.05	ND
Cs	1.8 ± 0.2	1.5 ± 0.2	2.3 ± 0.2	2.8 ± 0.3	1.8 ± 0.3
Ba	287 ± 35	339 ± 26	335 ± 30	514 ± 35	475 ± 32
Eu	0.4701 ± 0.1091	0.68 ± 0.09	0.9 ± 0.1	1.2 ± 0.1	0.6 ± 0.1
Yb	3.49 ± 0.16	2.5 ± 0.1	3.4 ± 0.1	3.7 ± 0.2	2.4 ± 0.1
Lu	0.36 ± 0.02	0.31 ± 0.02	0.45 ± 0.02	0.44 ± 0.02	0.29 ± 0.02
Hf	41.7 ± 0.5	31.1 ± 0.4	23.5 ± 0.4	21.8 ± 0.3	19.8 ± 0.4

ND: Not Detected

Reference

- [1] Verma, H.R., *Atomic and Nuclear Analytical Methods, XRF, Mössbauer, XPS, NAA and Ion-Beam Spectroscopic Techniques*, Punjabi University, Springer-Verlag Berlin Heidelberg, 2007, Ch 6, pp 243-268.
- [2] James, N. B., and Cynthia, M. L., *Applied Spectroscopy Review* **37**, 19–55 (2002)
- [3] Queirolo, F., Stegen, S., Restovic, M., Paz, M., Ostapczuk, P., Schwuger, M. J., Munoz, L. Total Arsenic, lead, and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. *The Sci. of the Total Environ.* 2000, 255:75.
- [4] Montoya, E. H., Cohen, R. I. M., Mendoza Hidalgo, P., Torres Chamorro, B. & Bedregal Salas, P. *Journal of Radioanalytical and Nuclear Chemistry* **240**, 1999, 475-479
- [5] De Corte, F. *Proefschrift, Rijksuniversiteit, Ghent*. 1987
- [6] Zhou Yongmao. IAEA-TECDOC-384 “Technology and Use of Low Power Research Reactors”. *Report of IAEA Consultants Meeting, Beijing, China 30 April – 3 May 1985*, pg 89-98
- [7] Jonah, S.A.; Balogun, G.I.; Umar, I.M.; Mayaki, M.C. Neutron Spectrum parameters in irradiation channels of the Nigeria Research Reactor – 1 (NIRR – 1) for k_0 – NAA standardization. *J. Radioanal. Nucl. Chem.* 266(1). 2005, 83 – 88.
- [8] Ahmed, Y.A., Ewa, I.O.B., Umar, I.M., Bezboruah, T., Johri, M., Akaho, E.H.K. The low power miniature neutron source reactors: Design, Safety and Applications. *IC/2006/020*
- [9] Sadiq, U., Jonah, S. A. Nasiru, R. and Zakari, Y. I. Neutron Spectrum Parameters in two irradiation channels of the Nigeria Research Reactor-1 (NIRR-1) for use in k_0 -NAA. *Bayero Journal of Pure and Applied Sciences*, 3(1): 2010, 220 – 223
- [10] Jonah, S.A.; Balogun, G.I.; Umar, I.M.; Oladipo, M.O.A.; Adeyemo D.J. Standardization of Nigeria Research Reactor – 1 (NIRR – 1) irradiation and counting facilities for instrumental neutron activation analysis. *Applied Radiation and Isotopes* 64. 2006, 818 - 822
- [11] Oladipo, M.O.A., Lori J.A., Bonire, J.J., and Ajayi, O. O. Trace element analysis of some shaving powders commonly marketed in Nigeria using Instrumental Neutron. *J. of Radioanalytical & Nuclear Chemistry, Vol. 224, Issue 1, 1997, pp 167 - 170*
- [12] Joseph, E., Nasiru, R. & Ahmed, Y. A. Trace Elements Pattern in some Nigerian Commercial Infant milk and Infant Cereal Formulas. *Annals of Biological Research*, 2(2), 2011, 351-360.
- [13] Adeleye, M. O., Ibrahim, Y. V., Njinga, R. L., Balogun, G. I. and Jonah, S. A. Determination of some metal contaminants from industrial effluents in North - West Nigeria using k_0 -NAA Standardization Method. *Advances in Applied Science Research*, 2012, 3 (2):678-684
- [14] Njinga, R.L., Jonah, S.A., Oladipo, M.O.A., Ewa, I.O.B.&Alfa, B. Use of k_0 -ENAA technique for Evaluation of Th, U and K in Sediments for Archaeometry Studies. *International Journal of Science and Technology Volume 1 No. 8, August, 2012. IJST © 2012 – IJST Publications UK. All rights reserved.* 391
- [15] McLaughlin, M. J. Bioavailability of Metals to Terrestrial Plants. In: Bioavailability of Metals in Terrestrial Ecosystems. Importance of partitioning for Bioavailability to Invertebrates, Microbes and Plants, Allen, H. E. (Eds.), *SETAC Press, Pensacola, FL*, 2001, pp: 39-68
- [16] Uchida, S., Tagami, K. and Hirai, I. Soil-to-plant transfer factors of stable elements and naturally occurring radionuclides: (2) Rice collected in Japan. *J. Nucl. Sci. Technol.*, 44: 2007, 779-790.
- [17] Rana, M. S., Halim, M. A., Saliullah, S., Mollah, M. M. and Azam, M. S. Removal of heavy metal from contaminated water by biopolymer crab shell chitosan. *J. Applied Sci.*, 9: 2009, 2762-2769
- [18] Underwood, E. J. *Trace Elements in Human and Animal Nutrition*, 3rd Edition, Academic Press, New York p. 116., 1971

- [19] Darby, W. J. *Trace elements in human health and disease*, Prasad AS and Oberleas D. Eds (Academic Press, New York, San Francisco, London) 1: 17, 1976
- [20] Gordon, R. F. *Poultry Diseases*. The English Language Book Society and Bailliere Tindall, London, 1977
- [21] Inuwa M, F.W. Abdurrahman, U. A Birnin Yauri and Ibrahim, S. A. Analytical determination of some trace metals in soils around the major industrial areas of north western Nigeria, *trends in applied sciences research*, 2007, 2(6)515-521
- [22] IITA. Selected Methods for Soil and Plant. Manual Series No:1, Ibadan,(1979)pp:2-50.
- [23] De Corte, F., Simonits, A., De Wispelaere, A., Hoste, J. Accuracy and applicability of the k_0 -standardization method. *J. Radioanal. Nucl. Chem.* 113 (1),1987, 145–161.
- [24] Joseph, E., Nasiru, R. Sadiq, U. & Ahmed, Y. A.. Energy and Efficiency Calibrations for High Purity Germanium GEM30195 Coaxial Detector USING k_0 -IAEA Software. *International Journal of Science and Research (IJSR)*, Volume 4 Issue 8, 2015, pp. 1056 – 1061
- [25] Blaauw, M., Bode, P., De Bruin, M. *Journal of Radioanalytical and Nuclear Chemistry, Articles*, 152 (2), 1991, 435-445.
- [26] Blaauw, M. The use of sources emitting coincident γ -rays for determination of absolute efficiency curves of highly efficient ge detectors. *Nuclear Instruments and Methods in Physics Research A* 332, 1993, 493-500.
- [27] Ewa, I.O.B. *Nigerian Journal of Physics*, 14 (1), 2004, 112-116.
- [28] Kolotov, V.P., De Corte F. *Pure Appl. Chem.* 76 (10), 2004, 1921-1925.
- [29] Rossbach, M., Blaauw, M., Bacchi, M.A., Xilei Lin. (2007). *Journal of Radioanalytical and Nuclear Chemistry*, 274 (3), 657-662.
- [30] FNB. "Dietary reference intakes for Vitamin A, Vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc," NAS/IOM(National Academy of Sciences/Institute of Medicine), Food and Nutrition Board, Institute of Medicine, Washington, DC.2003
- [31] Williams, U. *S.A Textbook of Biology*, Third Edition.1992
- [32] Wilkinson SR, Welch RM, Mayland HF, Grunes DL. Magnesium in plants: Uptake, distribution, function, and utilization by man and animals. *Metal Ions in Biological Systems* 26:1990, 33–56.
- [33] Drummond RSM, Tutone A, Li Y-C, Gardner RC. A putative magnesium transporter AtMRS2-11 is localized to the plant chloroplast envelope membrane system. *Plant Science* 170:2006, 78–89.
- [34] Waterlow, J. C. Protein Energy Malnutrition. London, Edwin Arnold.1992.
- [35] Classen, H. G. Magnesium and Potassium Deprivation and Supplementation in Animals and Man: aspects in view of intestinal absorption. *Magnesium*, 3:1984, 257-264.
- [36] Al-Ghamdi, S. M. Cameron, E. C. and Sutton, R. A. Magnesium Deficiency: pathophysiological and clinical overview. *Am. J. Kidney Dis.*, 24:1994, 737-754.
- [37] NAS/NRC. Arsenic in drinking water. NAS/NRC (National Academy of Sciences/National Research Council). Washington, DC.1999 pp. 251-257
- [38] Samac, D. A. & Tesfaye, M.. Plant improvement for tolerance to aluminium in acid soils. *Plant Cell, Tissue and Organ Culture*, 75, 2003, 189-207
- [39] Jovanovic, Z.; Djalovic, I.; Komljenovic, I.; Kovacevic, V. & Cvijovic, M. Influences of liming on vertisol properties and yields of the field crops. *Cereal Res. Commun.*, 34, 2006, 517-520
- [40] Jovanovic, Z.; Djalovic, I.; Tolimir, M. & Cvijovic, M. Influence of growing system and NPK fertilization on maize yield on pseudogley of Central Serbia. *Cereal Res. Commun.*, 35, 2007, 1325-1329
- [41] Barcelo, J. & Poschenrieder, C. Fast root growth responses, root exudates and internal detoxification as clues to the mechanisms of aluminium toxicity and resistance: A review. *Env. Exp. Bot.*, 48, 2002, 75–92
- [42] Silva, J. A. and Uchida, R. Essential Nutrients for Plant Growth: Nutrient Functions and Deficiency Symptoms. *Plant Nutrient Management in Hawaii's Soils, Approaches for Tropical and Subtropical Agriculture* J. A. Silva and R. Uchida, eds. College of Tropical Agriculture and Human Resources, University of Hawaii at Manoa, ©2000
- [43] Chapman, H. D. Ed., *Diagnostic Criteria For Plants and Soils*, University of California, Riverside, Calif, USA, 1972
- [44] Ure, A. M. & Bacon, J. R. "Comprehensive analysis of soils and rocks by spark-source mass spectrometry," *The Analyst*, vol. 103, no. 1229,1978, pp. 807–822.
- [45] Ahlrichs, J. L. "The soil environment," in *Organic Chemicals in the Soil Environment*, C. A. I. Goring and J.W. Hamaker, Eds., Marcel Dekker, New York, NY, USA, 1972
- [46] Tisdale, S. L., Nelson, W. L., Beaton, J. D. & Havlin, J. L. *Soil Fertility and Fertilizer*, Prentice Hall, Upper Saddle River, NJ, USA, 5th edition, 1993.
- [47] Perez-Benito, J. F. Effects of chromium (VI) and vanadium (V) on the lifespan of fish. *J. Trace Elem. Med. Biol.*, 20:2006, 161–170.
- [48] Schulte, E. E. *Soil and Applied Iron*, Understanding Plants Nutrients A3554, 2000
- [49] NAS/IOM. "Dietary reference intakes for Vitamin A, Vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc," NAS/IOM(National Academy of Sciences/Institute of Medicine), Food and Nutrition Board, Institute of Medicine, Washington, DC, 2003
- [50] Goyer, R.A., Clarkson T.M. Toxic effects of metals, In: Klaassen, C.D., ed Casarett & Doull's toxicology. New York: McGraw-Hill, 2001, pp. 811-868
- [51] Sandia Corporation. Chromium Background Soil Levels, 2000. <http://www.state.ma.us/dept/eeselector/gc/gc/na/chromiumsoillevels.html>
- [52] Daviscarter J.G., Shuman L. M. Influence of texture and pH of baolinitic soils on zinc fractions and zinc uptake by peanuts, *Soil Sci.* 155 (1993) 376–384.
- [53] Baker A.J.M. Ecophysiological aspects of zinc tolerance in *Silene maritima*, *New Phytol.* 80 (1978) 635–642.
- [54] Bradshaw A.D., McNeilly T. Evolution and Pollution, Edward Arnold, London, 1981
- [55] Doyar, M.A., Van Hai Tang. Effect of P, N and HCO₃ levels in the nutrient solution on rate of zinc absorption by rice roots and zinc content in plants. *Z. Pflanzenphysiol.* 98 (1980) 203–212.
- [56] Pearson J.N., Rengel Z. Uptake and distribution of ⁶⁵Zn and ⁵⁴Mn in wheat grown at sufficient and deficient levels of Zn and Mn. I. During vegetative growth, *J. Exp. Bot.* 46 (1995) 833–839.
- [57] Tucker, R. M. Essential Plant Nutrients: Their presence in North Carolina soils and role in plant nutrition. NCDA & CS, 1999.
- [58] Kabata, H. and Pendias, A. *Trace Elements in Soil and Plants*, (2nd Edn., Boca Boca Raton FL, USA, 365, Lewis, 1993)